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TITLE:

PURIFICATION OF PHOSPHORIC ACID  
PLANT POND WATER

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## **PURIFICATION OF PHOSPHORIC ACID PLANT POND WATER**

This application claims the benefit of U.S. Provisional Application entitled "Purification of Phosphoric Acid Plant Pond Water," Serial No. 60/353,359, filed October 25, 2001. This application is related to the application entitled "SIMPLIFIED  
5 PURIFICATION OF PHOSPHORIC ACID PLANT POND WATER," by applicants Dennis H. Michalski, et. al., filed concurrently herewith, and which is incorporated in its entirety herein by reference.

## **BACKGROUND OF THE INVENTION**

10 Production of phosphoric acid by what is commonly know as the "wet process" involves the reaction of finely ground phosphate rock with sulfuric acid. As a result of the various reactions, a slurry is produced containing phosphoric acid, calcium sulfate and various impurities derived from the phosphate rock. This slurry is normally filtered to separate the phosphoric acid product from the byproduct calcium sulfate. The  
15 phosphoric acid thus obtained is then used in the production of various phosphate fertilizers that are used in agriculture. Water is normally used to wash the calcium sulfate filter cake and thereby increase the recovery of the phosphoric acid product. Most of this wash water is fed back into the phosphoric acid production process as make-up water. However, a portion of this water remains trapped in the calcium sulfate filter cake and is  
20 discharged from the filter with the filter cake. This trapped water contains small amounts of phosphoric acid and small amounts of all other impurities that were present in the phosphoric acid product. Additional water is normally used to wash the calcium sulfate filter cake off of the filter and transport it, by pumping as a slurry, to a storage or disposal area.

25 At the storage or disposal area the calcium sulfate will settle and the excess water will be liberated. This liberated water will normally be collected in a system of channels and ponds and recycled to the phosphoric acid production plant for reuse (i.e., washing the calcium sulfate filter cake). These channels and ponds also serve as a collection means for other water that is used in and around the phosphoric acid plant, such as for  
30 cleaning or washing, fresh water fume scrubbers, and as a collection means for

phosphoric acid spills or leaks within the plant. Also, since these channels and ponds are located outside, they collect rain water.

Since all of the water contained within these channels and ponds contains small amounts of phosphoric acid and other impurities normally present in the phosphoric acid, it is considered contaminated. Thus, before this water can be released to the environment, it must be treated or purified to remove the phosphoric acid and other impurities. In some cases, in an efficiently operated phosphoric acid plant, in the absence of severe weather conditions, a balance will exist between water input to the pond system and water evaporation such that virtually all of this contaminated water can be recycled and used within the plant. In this case, treatment and discharge of the contaminated water, commonly known as pond water, is not necessary.

However, there are circumstances under which treatment and discharge of the contaminated pond water is necessary. One such circumstance could be an extended period of abnormally heavy rainfall. Another such circumstance would be when the phosphoric acid plant has ceased operation either for an extended period of time or permanently.

Many factors influence the specific components and their concentrations in this contaminated pond water. Thus, there is no typical composition for the pond water other than the fact that it will contain some phosphate. However, some of the chemical components that could be found in pond water, and an example of their range of concentrations, are as follows:

| <u>CHEMICAL COMPONENT</u> | <u>RANGE OF CONCENTRATION</u> |
|---------------------------|-------------------------------|
| P                         | 1700-12,000 ppm               |
| SO <sub>4</sub>           | 4300-9600 ppm                 |
| F                         | 200-15,000 ppm                |
| Si                        | 100-4100 ppm                  |
| (ammoniacal) N            | 40-1500 ppm                   |
| Na                        | 1200-2500 ppm                 |
| Mg                        | 160-510 ppm                   |
| Ca                        | 450-3500 ppm                  |

|    |            |
|----|------------|
| K  | 80-370 ppm |
| Fe | 5-350 ppm  |
| Al | 10-430 ppm |
| Cl | 10-300 ppm |

One method of treating or purifying this pond water well known in the art is double liming. This method consists of adding a calcium compound (such as  $\text{CaCO}_3$ ,  $\text{Ca(OH)}_2$  or  $\text{CaO}$ ) to the pond water, in two stages, such that the phosphate and other impurities form solid precipitates that settle and are separated from the thus purified water. This method is described in Francis T. Nielsson, ed., *Manual of Fertilizer Processing*, Marcel Dekker, Inc. (1987), pp. 480 to 482; G.A. Mooney, et al., *Removal of Fluoride and Phosphorus from Phosphoric Acid Wastes with Two Stage Line Treatment*, Proceedings of the 33rd Industrial Waste Conference, Purdue Univ. (1978); G.A. Mooney et al., *Laboratory and Pilot Treatment of Phosphoric Acid Wastewaters*, presented at the Joint Meeting of Central Florida and Peninsular, Florida A.I.Ch.E. (1977); and U.S. Patent Nos. 5,112,499; 4,698,163; 4,320,012; 4,171,342; 3,725,265 and 3,551,332. However, there are several problems associated with this method. One problem is the large volume of sludge produced. Sludge (i.e., a mixture of the precipitated impurities, un-reacted calcium compound and water) is produced in both the first and second stages of this process. These sludge materials are normally deposited in settling ponds that require large land areas. While it is possible to reclaim and recycle some of the sludge from the first stage of this process, the sludge from the second stage tends to be very voluminous, extremely difficult to de-water and of little economic value. Thus, large impoundment ponds are required to permanently store this sludge. Another problem with this method of pond water treatment is that, because of the large quantity of water tied up with the sludge, only about 50% to 60% of the pond water fed to the process can be discharged. Thus, the process equipment must be significantly larger than would otherwise be needed. A third problem with this process is that virtually all of the economically valuable phosphate contained in the pond water is converted to a form that renders it unsuitable for use as a fertilizer without significant re-processing at added cost. Finally, a fourth problem with this treatment process is that the purified pond water often just

barely meets the criteria for discharge and cannot be used as a substitute for the fresh water that would normally be required in a phosphoric acid plant, such as for steam production.

Another general method of water purification is reverse osmosis. This process is based on the application of external pressure on an aqueous salt solution in contact with a semi permeable membrane, such that the applied pressure exceeds the osmotic pressure of the water component of the solution in contact with the membrane. Thus, some of the water is forced through the membrane in the reverse direction, while the other components in the solution (i.e., soluble salts) do not pass through the membrane. This results in a stream of purified water, known as permeate, and a stream of increased salt content, known as the reject or concentrate. Reverse osmosis is well known in the art and is described in Douglas M. Ruthven, ed., *Encyclopedia of Separation Technology*, Volume 2, pp. 1398-1430, John Wiley & Sons, Inc. (1997); S. Sourirajan and T. Matssuura, *Reverse Osmosis/Ultrafiltration Principles*, National Research Council of Canada, Ottawa, Canada (1985); B. Parekh, ed., *Reverse Osmosis Technology*, Marcel Dekker, Inc., New York (1988); R. Rautenbach and R. Albrecht, *Membrane Processes*, John Wiley & Sons, Inc., New York (1989) and other publications. Reverse osmosis is also described in a variety of U.S. Patents, for example, U.S. Patent Nos. 4,110,219; 4,574,049; 4,876,002; 5,006,234; 5,133,958 and 6,190,558.

Several attempts have been made to use reverse osmosis for the purification of contaminated phosphoric acid plant pond water. However, these attempts have generally failed due to the fact that the pond water is a saturated solution. Thus, as soon as any water is removed from the pond water the solution becomes supersaturated and salts precipitate that quickly clog the membranes used in reverse osmosis and prevent additional pure water from flowing through them.

However, if reverse osmosis could be made to function in the treatment of contaminated phosphoric acid plant pond water, many economic and environmental benefits would result. One benefit is that the phosphate values contained in the pond water would be recovered in an economically useful form (i.e., as a concentrated liquid phosphate solution). Another benefit is that vast land areas required for the settling ponds needed in the double liming process will be greatly reduced and the large

impoundment ponds needed for permanent sludge storage will be eliminated. A third benefit is that the purified water obtained from the reverse osmosis system is of sufficient purity such that it can be used in place of fresh water in places where fresh water is required (i.e., certain fume scrubbers, steam boiler feed systems, etc.). Still other benefits will be obvious to those skilled in the art.

### **SUMMARY OF THE INVENTION**

It is an object of this invention to provide a process for the pre-treatment of contaminated phosphoric acid plant pond water (hereinafter called "pond water") such that the pre-treated pond water can be purified using conventional reverse osmosis technology.

It is another object of this invention to provide a process for the pre-treatment or partial purification of pond water such that the pre-treated pond water can be concentrated by the removal of pure water, using any suitable apparatus, without the formation of solid precipitates in the solution thus concentrated.

It is another object of this invention to provide a process for the partial purification of pond water such that the partially purified pond water can be processed by a conventional reverse osmosis system continuously without the precipitation of compounds within the reverse osmosis system that would clog the membranes employed within the system rendering them inoperative.

It is another object of this invention to provide a process for the selective removal of specific ions and compounds from pond water to an extent such that the thus processed pond water can be further processed by a conventional reverse osmosis system to produce a permeate stream composed of essentially pure water and a reject or concentrate stream composed of the phosphate component and other impurities present in the processed pond water fed to the reverse osmosis system.

It is also an object of this invention to provide a process for the purification of pond water that will significantly reduce the quantity of undesirable sludge that is generated.

These and other objects are achieved by the present invention which provides a process for partial purification pre-treatment of pond water comprising the steps of

adding a first compound that will react with the fluorides in the pond water and form an essentially insoluble fluoride salt, adding a second compound that is either basic or will form a base when water is present, the cationic portion of said second compound being such that the phosphate salts thereof remain soluble, allowing the precipitates thus  
5 formed to settle, decanting or otherwise separating the clarified liquid portion of the mixture, holding the liquid portion of the mixture for a time period sufficient to allow the silicic acid present to decompose into hydrated silicon dioxide, separating the hydrated silicon dioxide and adding an acid to the liquid solution thus obtained, such that the solubility of the ions remaining in solution are increased and are greater than or equal to  
10 their concentrations that are expected in the thus treated solution when the solution is concentrated via the removal of essentially pure water.

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The present invention provides a process for partially purifying contaminated  
15 phosphoric acid plant pond water such that the partially purified or pre-treated pond water can be concentrated by the removal of pure water without the formation of precipitated solids or scale that would otherwise impede or render inoperable the concentrating means or apparatus. Thus, for example, the pre-treated pond water could be processed through a conventional reverse osmosis system comprising one or more  
20 stages to obtain a purified water stream and a stream of concentrated pond water. The term "pond water," as used herein, is defined as a dilute solution of phosphoric acid, also containing sulfuric acid, silicic acid, fluoride ions, calcium ions, sodium ions, ammonium ions, and other ionic and non-ionic species, that is normally present in and around phosphate fertilizer plants that employ the so-called wet process for the production of  
25 phosphoric acid.

In the process of the present invention, a first compound is added to the pond water that will react with the fluorides in the pond water and form an essentially insoluble fluoride salt. Several compounds of this type include magnesium containing compounds, calcium containing compounds, strontium containing compounds and barium containing  
30 compounds. Of particular utility, due to their low cost, are the calcium containing compounds including calcium carbonate, calcium hydroxide and calcium oxide. The

quantity of said compound added to the pond water is based on the fluorine concentration in the pond water such that the molar ratio of the cationic portion of the compound to the fluorine in the pond water is within the range of 0.45 to 0.80, or more preferably within the range of 0.50 to 0.70, or still more preferably within the range of 0.55 to 0.65. Thus, if the quantity of fluorine contained in the pond water to be treated were 19 pounds and the compound to be added were calcium oxide, the quantities of calcium oxide corresponding to the three ranges stated above would be about 25.2 - 44.9 pounds, 28.0 - 39.2 pounds and 30.8 - 36.4 pounds. This first compound can be added to the pond, water either in dry form, as a paste or as a liquid slurry, and still be within the scope of the present invention. Furthermore, this first compound can be added to the pond water either on a batch basis or on a continuous basis and still be within the scope of the present invention. This first compound is mixed with the pond water for a time period sufficient for the compound to react with the fluorine in the pond water. Typically, this time period will be from 1 minute to 30 minutes, depending on the form in which the compound is added to the pond water and the configuration of the mixing apparatus.

After the first compound has been mixed with the pond water for a sufficient time, the mixture can be clarified and the solids formed as a result of reactions of the first compound with the pond water can be removed. In practice slightly better results are obtained if the solids formed as a result of reactions of the first compound with the pond water are left in the pond water. However, removal of these solids at this point is still considered within the scope of the present invention.

A second compound is now added to the pond water. If the pond water is being treated on a batch basis and the solids produced as a result of the reactions of the first compound with the pond water are not removed, this second compound can be added in the same vessel. If the pond water is being treated on a continuous basis, the pond water, with or without the reaction products from the first compound addition, must be transferred to a second tank or vessel. The second compound must be a strong base or a compound that will form a strong base when water is present. Furthermore, the cationic component of the second compound must be such that the phosphate salts formed thereof remain soluble in the pond water. Examples of strongly basic compounds that form



soluble phosphate salts include sodium hydroxide and potassium hydroxide. An example of a compound that will form a strong base when water is present and whose phosphate salt is soluble is ammonia. Other compounds meeting the above two criteria may also be used and are still considered within the scope of the present invention. The second

5 compound is added to and mixed with the pond water, either in pure form or as a solution, in sufficient quantity to increase the pH of the resulting pond water solution to a value within the range of 4.2 to 8.0, or more preferably within the range of 5.0 to 6.5, or still more preferably within the range of 5.5 to 6.0. The term "pure form," as used above, refers to the physical state of the compound (i.e., a solid for sodium hydroxide or

10 potassium hydroxide, or a gas or pressurized liquid for anhydrous ammonia) and not the chemical purity of the compound. In terms of chemical purity, ordinary technical grade purity is acceptable for both the first compound and the second compound.

The pH, as used above and elsewhere, is defined as the negative power to which 10 must be raised to equal the molar hydrogen ion concentration in solution.

15 As a result of the addition of the first compound and second compound to the pond water and the resulting chemical reactions, solid precipitates will form in the solution. These solid precipitates are now removed from the solution either by settling the solids and decanting the liquid, centrifuging the solution, filtering the solution, or any other means that will result in a separation of a clear liquid from the solid precipitates.

20 Furthermore, it is not necessary that all of the liquid be removed from the solids. Thus, the solids can be removed as a slurry containing, for example, 50% by weight solids and 50% by weight liquid. Also, it is not essential that all of the solids be removed from the liquid, although it is preferred that the suspended solids concentration in the liquid be no greater than 0.5% by weight.

25 If the clear liquid thus obtained is subjected to chemical analysis, it will be found that the calcium and fluorine concentrations have been significantly reduced, as compared to the starting pond water, while the phosphate concentration has only been reduced by a comparatively minor amount.

The clear liquid is now allowed to age. The purpose of the aging is to allow

30 silicic acid present in the liquid to decompose into hydrated silicon dioxide. The aging time should be at least 2 hours and preferably at least 16 hours. While there is no upper

limit to the aging time, and longer aging times have been found to be beneficial, practicality and economics dictate that the maximum aging time would normally be limited to about 10 days or less.

After the aging period, the hydrated silicon dioxide formed as a result of the aging process must be removed from the liquid. This can be done by any conventional solid liquid separation technique including centrifuging, filtering or settling. Of particular utility is the use of a flocculent, specifically a cationic flocculent, followed by settling of the flocculated silicon dioxide and decantation of the liquid. The quantity of flocculent required and the method of addition will depend, among other factors, on the concentration of hydrated silicon dioxide in the liquid and the specific flocculent used. Thus, laboratory tests, by techniques well known in the art, would be required to determine the flocculent addition parameters. The use of a flocculent for hydrated silicon dioxide removal is not considered a part of the present invention and is presented only to illustrate a useful means of accomplishing the part of the present invention comprising silica removal from the partially pre-treated pond water. The use of flocculants for silica removal is taught in U.S. Patents Nos. 5,595,717; 5,453,206; 5,409,614 and 5,200,165.

At this point in the process, the majority of the calcium, fluorine and silica, originally present in the pond water have been removed. Thus, the pond water has been partially purified.

After the removal of the hydrated silicon dioxide, a clear liquid is obtained that is essentially saturated with respect to various ions and salts thereof. To permit the removal of pure water from this liquid solution, without causing precipitation of these salts, the solubility relationships of these salts within the solution must be adjusted. This is accomplished by adding an acid to the solution, or a compound that will form an acid when water is present, so as to cause a decrease in the pH. A method of decreasing the pH by the addition of an acid is taught in U.S. Patent No. 5,338,456. However, in the process described in U.S. Patent No. 5,338,456 the acid is added to convert carbonates (for example calcium carbonate) to carbon dioxide such that the carbon dioxide can be removed from the water in the forced draft and vacuum degasifiers. Thus, the net effect of the acid addition in U.S. Patent No. 5,338,456 is to decrease the solubility of the carbon compounds in solution and not to increase the solubility of the various ions and

salts present, as is the purpose of the acid addition in the pond water of the present invention. Examples of acids that may be used include sulfuric acid, sulfurous acid, phosphoric acid, hydrochloric acid and nitric acid. Examples of compounds that may be used that will form an acid when water is present include sulfur trioxide, sulfur dioxide, hydrogen chloride and nitrogen dioxide. Other acids, or compounds that will form acids in the presence of water, may be used and are still considered within the scope of the present invention. Acids that should not be used for pH adjustment include hydrofluoric acid and hydrofluorosilicic acid. The acid or the compound that will form an acid in the presence of water should be added to the liquid in sufficient quantity to decrease the pH of the resulting solution to a value within the range of 2.0 to 4.0, or more preferably within the range of 2.5 to 3.5, or still more preferably within the range of 2.9 to 3.1.

The liquid solution thus obtained will be essentially clear and stable with respect to post precipitation. In addition, pure water may now be removed from the liquid solution by any of several methods including reverse osmosis, evaporation, or other means, without the formation of solid precipitates.

The process of this invention will be better understood with reference to the following examples. It is understood, however, that these examples are intended only to illustrate the invention and are not intended to limit the invention. All percentages used in the following examples, unless noted otherwise, are understood to mean percent by weight.

#### EXAMPLE 1

A 3780 gram sample of contaminated phosphoric acid plant pond water containing 1.85%  $P_2O_5$ , 0.121% Ca, 0.360% F, 0.074% Si and 0.425%  $SO_4$  was obtained from a commercial wet process phosphoric acid plant pond system. To this sample, 17.3 grams of calcium oxide was added and the solution was mixed for about 20 minutes. Next, 50% sodium hydroxide solution was added to and mixed with the above solution in the amount of 42.16 grams, which was sufficient to increase the pH to 5.0. The solution was then allowed to stand, whereupon the solids precipitated as a result of the chemical reactions between the calcium oxide, sodium hydroxide and pond water settled to form a sludge at the bottom of the container. After 16 hours, 3524 grams of clear liquid was

decanted from the above container, leaving a sludge that represented 8.22% by weight of the initial pond water, calcium oxide and sodium hydroxide solution. The clear liquid was then allowed to age for an additional 32 hours. At this point, the liquid had a somewhat hazy appearance as a result of the decomposition of the silicic acid present in the hydrated silicon dioxide. Flocculent was then added to and mixed with a 1750 gram sample of the above aged solution in an amount equal to 0.41 grams. The flocculent used was produced by Arr-Maz Products, LP and was designated 1046C. The solution was then allowed to stand 5 hours, whereupon the flocculated silicon dioxide settled to form a sludge at the bottom of the container. After 5 hours, 1350 milliliters of clear liquid was decanted from the above container, leaving a sludge that represented about 23% by volume of the original 1750 gram sample. The pH of the resulting clear liquid was then adjusted to a value of 3.01 via the addition of 1.99 grams of 96% sulfuric acid. Laboratory analysis of a sample of the solution at this point indicated that it contained 1.50%  $P_2O_5$ , 0.0064% Ca, 0.0202% F and 0.0027% Si.

A 900 gram sample of this solution was then placed in a beaker on a laboratory stirrer-hotplate and heat was applied while stirring the solution to evaporate water. This process was continued until the final weight of the solution was 103 grams, thus indicating that 797 grams of water had been evaporated. At this point, the remaining solution was still clear with no evidence of precipitated solids. Laboratory analysis of a sample of the evaporated solution indicated that it now contained 7.41%  $P_2O_5$ , 0.0392% Ca, 0.121% F and 0.023% Si.

### EXAMPLE 2

A 226 gallon sample (1,917 pounds) of pond water containing 1.61%  $P_2O_5$ , 0.119% Ca, 0.470% F, 0.084% Si, 0.440%  $SO_4$ , and 0.230% Na was used for this test. To this sample, 17.64 pounds of calcium oxide was added and the solution was mixed for about 30 minutes. Next, 50% sodium hydroxide solution was added to and mixed with the above solution, in the amount of 21.34 pounds, which was sufficient to increase the pH to 5.6. The solution was then allowed to stand, whereupon the solids, precipitated as a result of the chemical reactions between the calcium oxide, sodium hydroxide and pond water, settled to form a sludge at the bottom of the container. After about 4 hours, about

206 gallons of clear liquid was decanted from the reaction tank into a second tank. After correcting for the volume of clear liquid not removed from the reaction tank, the remaining sludge amounted to 3.54% by volume of the initial 226 gallons of pond water.

The clear liquid was then allowed to age for an additional 36 hours. Two flocculants were then added, in series, to the 206 gallons of liquid in the second tank. The first flocculent, designated 1018C, was added in an amount equal to 150 parts per million by weight and mixed for approximately 3 minutes. The second flocculent, designated 811E, was then added in an amount equal to 8 parts per million by weight and mixed for approximately 30 seconds. Both flocculants were produced by Arr-Maz Products, LP.

The solution was allowed to stand for about 1 hour and then about 170 gallons of clear liquid was decanted from the second tank into a third tank. After correcting for the volume of clear liquid not removed from the second tank, the remaining silicon dioxide sludge amounted to 7.28% by volume based on the initial volume of 226 gallons of pond water. The pH of the resulting 170 gallons of clear liquid was then adjusted to a value of 3.0 via the addition of 2.44 pounds of 97.35% sulfuric acid. Laboratory analysis of a sample of the solution at this point indicated that it contained 1.17%  $P_2O_5$ , 0.0102% Ca, 0.0114% F, 0.0070% Si, 0.482% Na and 0.530%  $SO_4$ . At this point, the total quantity of sludge produced by the partial purification process of the present invention was 10.82% by volume of the starting pond water or 24.45 gallons.

The above 170 gallon sample of the pre-treated, partially purified pond water, prepared according to the process of the present invention, was then processed through a conventional, two stage reverse osmosis system. The first stage reverse osmosis module contained a conventional sand filter, a 5-micron cartridge filter, a feed tank, a 5-HP positive displacement high-pressure pump and a single membrane element. The membrane element used in the first stage module was a seawater element with the U.S. Filter designation SW2530. The operating conditions for the first stage reverse osmosis module were an inlet pressure of 850 psi (pounds per square inch), a temperature of 102° F. and a permeate recovery of about 80.6% by volume. Thus, the first stage reverse osmosis module produced about 137 gallons of purified permeate and about 33 gallons of reject or concentrate. Laboratory analysis of the permeate indicated that it contained 0.0036%  $P_2O_5$ , 0.0017% Ca, 0.0045% F, 0.0005% Si, 0.0572% Na and 0.0115%  $SO_4$ .

Laboratory analysis of the reject stream indicated that it contained 5.65%  $P_2O_5$ , 0.0429% Ca, 0.0379% F, 0.0369% Si, 2.144% Na and 2.830%  $SO_4$ .

The 137 gallons of permeate obtained from the first stage reverse osmosis module were mixed with about 0.55 pounds of 50% sodium hydroxide to raise the pH to a value of about 9. This solution was then fed to the second stage reverse osmosis module. The second stage reverse osmosis module contained essentially the same components as the first stage reverse osmosis module with the exception of the sand filter. The membrane element used in the second stage module was a brackish water element with the U.S. Filter designation BW2530. The operating conditions for the second stage reverse osmosis module were an inlet pressure of 195 psi (pounds per square inch), a temperature of 85° F. and a permeate recovery of about 94.5% by volume. The second stage reverse osmosis module produced about 130 gallons of permeate and about 6.8 gallons of reject or concentrate. Laboratory analysis of the permeate from the second stage module indicated that it contained 0.00005%  $P_2O_5$ , <0.00001% Ca, 0.00008% F, 0.0001% Si, 0.0008% Na and <0.0001%  $SO_4$ . Laboratory analysis of the reject stream indicated that it contained 0.0680%  $P_2O_5$ , 0.00002% Ca, 0.0515% F, 0.0028% Si, 0.1370% Na and 0.0300%  $SO_4$ .

Thus, after correcting for the volumes of partially pre-treated pond water intentionally not recovered during the two sludge separation steps (the CaO/NaOH sludge and the hydrated silicon dioxide sludge), the pretreatment process of the present invention allowed the recovery of about 72.1% by volume of the initial pond water as essentially pure water in the second stage reverse osmosis permeate stream and the recovery of about 68.5% of the  $P_2O_5$  in the initial pond water as an economically valuable solids free solution in the first stage reverse osmosis reject stream.

### EXAMPLE 3

A 206 gallon sample (1,718 pounds) of pond water containing 1.57%  $P_2O_5$ , 0.111% Ca, 0.500% F, 0.094% Si, 0.460%  $SO_4$ , and 0.230% Na was used for this test. To this sample, 19.82 pounds of calcium oxide was added and the solution was mixed for about 30 minutes. Next, anhydrous ammonia was injected below the liquid surface and mixed with the above solution in the amount of 3.19 pounds, which was sufficient to

increase the pH to 5.6. The solution was then allowed to stand, whereupon the solids precipitated as a result of the chemical reactions between the calcium oxide, anhydrous ammonia and pond water settled to form a sludge at the bottom of the container. After about 4 hours, about 180 gallons of clear liquid was decanted from the reaction tank into a second tank. After correcting for the volume of clear liquid not removed from the reaction tank, the remaining sludge amounted to 3.40% by volume of the initial 206 gallons of pond water. The clear liquid was then allowed to age for an additional 120 hours. Two flocculants were then added, in series, to the 180 gallons of liquid in the second tank. The first flocculent, designated 1018C, was added in an amount equal to 100 parts per million by weight and mixed for approximately 3 minutes. The second flocculent, designated 811E, was then added in an amount equal to 8 parts per million by weight and mixed for approximately 30 seconds. Both flocculants were produced by Arr-Maz Products, LP. The solution was then allowed to stand for about 1 hour and then about 120 gallons of clear liquid were decanted from the second tank into a third tank. After correcting for the volume of clear liquid not removed from the second tank, the remaining silicon dioxide sludge amounted to 13.3% by volume based on the initial volume of 206 gallons of pond water. The pH of the resulting 120 gallons of clear liquid was then adjusted to a value of 3.0 via the addition of 1.62 pounds of 97.35% sulfuric acid. Laboratory analysis of a sample of the solution at this point indicated that it contained 1.01%  $P_2O_5$ , 0.0102% Ca, 0.0139% F, 0.0042% Si, 0.150%  $NH_3$  and 0.540%  $SO_4$ . At this point, the total quantity of sludge produced by the partial purification process of the present invention was 16.7% by volume of the starting pond water or 34.4 gallons.

The above 120 gallon sample of the pre-treated, partially purified pond water, prepared according to the process of the present invention, was then processed through a conventional, two stage reverse osmosis system. The system components and membrane elements were the same as were used in Example 2, above. The operating conditions for the first stage reverse osmosis module were an inlet pressure of 390-675 psi (varied during the test), a temperature of about 103° F. and a permeate recovery of 71% to 80.5% (varied as a function of inlet pressure) by volume. The first stage reverse osmosis module produced a total volume, at all test conditions run, of about 96.6 gallons of

purified permeate and about 23.4 gallons of reject or concentrate. Laboratory analysis of the permeate indicated that it contained 0.0047%  $P_2O_5$ , <0.0001% Ca, 0.0039% F, 0.0001% Si, 0.0014%  $NH_3$  and 0.0027%  $SO_4$ . Laboratory analysis of the reject stream indicated that it contained 4.56%  $P_2O_5$ , 0.0429% Ca, 0.0452% F, 0.0318% Si, 0.650%  $NH_3$  and 2.847%  $SO_4$ .

The 96.6 gallons of permeate obtained from the first stage reverse osmosis module were mixed with about 0.39 pounds of 50% sodium hydroxide to raise the pH to a value of about 9. This solution was then fed to the second stage reverse osmosis module. The operating conditions for the second stage reverse osmosis module were an inlet pressure of 150 psi (pounds per square inch), a temperature of 90° F. and a permeate recovery of about 85.5% by volume. The second stage reverse osmosis module produced about 82.7 gallons of permeate and about 13.9 gallons of reject or concentrate. Laboratory analysis of the permeate from the second stage module indicated that it contained 0.00016%  $P_2O_5$ , <0.00001% Ca, 0.00016% F, 0.00002% Si, 0.00058%  $NH_3$  and 0.0001%  $SO_4$ . Laboratory analysis of the reject stream indicated that it contained 0.0317%  $P_2O_5$ , 0.0005% Ca, 0.0259% F, 0.0004% Si, 0.0061%  $NH_3$  and 0.0184%  $SO_4$ .

Thus, after correcting for the volumes of partially pre-treated pond water intentionally not recovered during the two sludge separation steps (the  $CaO/NH_3$  sludge and the hydrated silicon dioxide sludge), the pretreatment process of the present invention allowed the recovery of about 64.4% by volume of the initial pond water as essentially pure water in the second stage reverse osmosis permeate stream and the recovery of about 70.8% of the  $P_2O_5$  in the initial pond water as an economically valuable solids free solution in the first stage reverse osmosis reject stream.

#### EXAMPLE 4 (Comparison)

A laboratory test of the prior art method of double liming was run. The results are presented as a basis of comparison to the process of the present invention. This method consists of adding  $CaO$  or  $Ca(OH)_2$  to the pond water until a pH of 5.0 to 5.5 is obtained. The sludge that forms as a result of the reactions between the pond water and  $CaO$  or  $Ca(OH)_2$  is then allowed to settle and the clear liquid is decanted. Additional  $CaO$  or  $Ca(OH)_2$  is then added to the clear liquid until a pH of 11.5 to 12.0 is obtained.



Additional sludge is produced and this sludge is also allowed to settle and the clear liquid is decanted. Typically, this clear liquid would then be analyzed and discharged if it met the legal discharge criteria.

A 3000 gram sample (2950 milliliters) of pond water containing 1.84%  $P_2O_5$ , 0.1072% Ca, 0.310% F and 0.460%  $SO_4$  was used for this test. To this sample, 48.2 grams of  $Ca(OH)_2$  was added to obtain a pH of 5.31. The solids produced as a result of the reactions between the pond water and  $Ca(OH)_2$  were then allowed to settle for 16 hours. Clear liquid, in the amount of 2529 grams (2555 milliliters), was then decanted, leaving a first stage sludge volume of 395 milliliters (13.4% by volume). Additional  $Ca(OH)_2$ , in the amount of 30.0 grams, was then added to the clear liquid to obtain a pH of 11.8. This solution was then allowed to stand for 3 days, after which 1715 milliliters of clear liquid was decanted, leaving 840 milliliters of additional sludge. Laboratory analysis of the clear liquid indicated that it contained 0.00045%  $P_2O_5$  and 0.0007% F, which are believed to be within the legal criteria for discharge.

Thus, while the pretreatment process of the present invention, as illustrated in Examples 2 and 3 above, allowed 72.1% and 64.4%, respectively, of the starting pond water to achieve discharge criteria, the quantity of starting pond water meeting discharge criteria using the prior art treatment process was only 58.1%. Also, using the pretreatment process of the present invention, 68.5% (Example 2) and 70.8% (Example 3) of the  $P_2O_5$  contained in the starting pond water was recovered in an economically useful form, while all of the  $P_2O_5$  was lost in the sludge waste streams using the prior art double liming process. Finally, using the pretreatment process of the present invention, the total quantities of waste sludge produced were only 10.82% (Example 2) and 16.7% (Example 3), by volume, of the starting pond water, while the total sludge using the prior art process was 41.9% of the starting pond water volume.

Although the present invention has been described in connection with specific examples, it is to be understood that various modifications are possible and this invention is to be limited only by the scope of the appended claims.